ENAMELS

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COMPARATIVE TESTING OF ONE-COAT ENAMELS FOR PIPES

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Comparative testing of industrially produced enamels and synthesized fluorine-free one-coat enamels was carried out. It was established that fluorine-free enamels of new compositions in certain properties (firing interval, chemical resistance, impact strength, etc.) exceed the existent analogs. The enamels are environmentally safe, have been subjected to extensive industrial testing, and have been accepted for production at various companies manufacturing steel pipes with enameled inner surfaces.

In large-scale production, such as enameling of steel pipes, the economic parameters, i.e., the cost and availability of raw materials, and the level of the complication of technology acquire great importance. Therefore, special attention is paid to the technology of one-coat enameling, which allows for savings in fuel, electricity, and materials, compared with the traditional technology of multi-layer coating. According to certain researchers, the saving in direct-on enameling reaches 50% [1].

Apart from the economic aspect, in selecting an enameling technology one should be guided by its environmental safety aspect. In particular, in the development of new direct-on enamels, it is necessary to eliminate the components which may be dangerous to human health. This is especially true of the fluorides widely used in one-coat enameling, as they belong to the contaminants of the first type [2].

Many countries, in order to improve the environmental situation, have adopted laws restricting atmospheric emissions of toxic components, including fluorine. Maximum permissible values were established not only for emissions, but for the concentrations of toxic agents in the atmosphere [3].

At present, the manufacturers of steel pipes with protection from corrosion use one-coat domestic and foreign enamels of grades 25, 20Ts, L-16, 90s, 155, etc., which all have specific limited application areas (Table 1). Thus, enamel 20Ts is used for cold and hot water pipelines, enamel 25 for alimentary equipment pipes and fittings, and enamels 90s and 155 for oil pipelines. Moreover, a serious drawback of the specified enamels is the presence of fluoric compounds in their compositions, which makes the processes of frit preparation and enameling environmentally unsafe. Therefore, the problem of developing environmentally safe enamels for one-coat enameling of pipes has become a pressing one. Such enamels should have better service characteristics than the existent ones, so that they could be used as protection for the inner surface of pipelines transporting any aggressive media, including cold and hot water.

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TABLE 1

Enamel	Mass content,* %													
	SiO_2	B_2O_3	Na_2O	K_2O	Li_2O	CaO	CaF_2	Al_2O_3	Fe_2O_3	MnO_2	TiO_2	Co_2O_3	Ni_2O_3	CuO
25	58.08	4.40	13.31	2.70	3.90	2.40	4.15	2.65	–	–	2.10	0.71	0.74	–
20Ts	60.00	7.00	13.00	4.00	3.50	0.60	5.10	–	–	1.20	–	0.60	–	–
L-16	55.00	5.00	14.60	–	3.00	–	5.80	0.50	5.0	1.00	7.10	1.00	–	–
90s	41.70	10.70	14.50	–	–	–	14.70	0.60	1.90	2.80	–	0.30	1.40	1.00
155	60.80	4.90	14.60	2.40	–	1.50	7.40	–	1.00	2.10	2.40	0.60	0.90	1.40

* Besides, enamel 25 contained 1.50% SrO and 3.36 Na_2SiF_6, enamel 20Ts contained 5.00 ZrO_2, enamel L-16 contained 2.00 ZnO, and enamel 90s contained 10.40 BaO.

TABLE 2

Parameters	Industrially produced enamel						Fluorine-free enamel	
	90s	25	20Ts	L-16	155	25Ts	ÉST-2	ÉST-7
				Frit				
Spreadability, mm	56.0	52.0	46.0	48.0	54.0	43.0	48.0 – 52.0	46.0 – 48.0
Water resistance by GOST 10134.1–82, class	3/98	3/98	2/98	2/98	2/98	2/98	2/98	1/98
Acid resistance in 20% HCl solution in 2-h boiling, %	1.28	0.98	0.58	1.33	1.14	1.32	0.20 – 0.26	0.10 – 0.16
				Coating				
Firing interval, °C	60	60	80	80	60	30	120	140
Resistance, mg/cm^2:								
in 20% HCl in 4-h boiling	1.92	0.65	0.45	0.89	0.85	0.52	0.12 – 0.25	0.009 – 0.019
in 4% NaOH solution at 80°C in 4-h boiling	1.48	0.59	0.62	0.52	0.92	0.60	0.15 – 0.19	0.10 – 0.13
in distilled water in 48-h boiling	0.65	0.45	0.50	0.92	0.68	0.50	0.05 – 0.07	0.04 – 0.05
Heat resistance, °C	120	180	180	140	140	160	260	280

We have developed one-coat enamels ÉST-2 and ÉST-7 which do not contain fluorine and fluoric compounds (RF Patent No. 2116271). The determination of the optimum ratio of the low-melting and high-melting components in enamels made it possible to obtain coatings whose physicochemical and thermomechanical properties meet the requirements imposed on inner protective coatings for steel pipelines of various purposes.

Fluorine-free enamels are produced by the standard technology. The batch is prepared from sand, borax, soda, chalk, alumina, potassium and sodium saltpeter, strontium and lithium carbonates, and titanium, zirconium, manganese, cobalt, nickel, and ferric oxides satisfying technical conditions and standards. Enamels are melted at 1280 – 1320°C for 2 – 2.5 h, and the degree of readiness is determined by filament and tablet. Granulation is carried out in water with subsequent drying of frit.

The synthesized enamels are subjected to wet grinding with the following additives to 100 weight parts of frit (weight parts): 5 – 25 quartz sand, 5 – 6 Chasovyarskoe clay, 0.3 – 0.5 borax, 0.2 – 0.4 soda, 0.2 – 0.3 ammonium molybdate, 0.2 – 0.5 sodium nitrite, 40 – 50 water. After grinding, the slips are left maturing, in order to average their characteristics and stabilize their properties.

The technological parameters of one-coat fluorine-free enamel slips are as follows: milling fineness (by Lisenko) 12 – 15 units, volume weight 1.67 – 1.78 g/cm^3, consistence 6 – 10 g/dm^2.

The developed direct-on enamels have good technological properties: enamel slips based on them have no tendency for thixotropy; they are applied to metal surface in a uniform layer without swelling and bulges; after firing they form a one-layer, well-fused, defect-free coating 0.25 – 0.50 mm thick with good continuity and luster (luster not less than 50%). The synthesized enamels have better physicochemical parameters than industrially produced enamels (Table 2).

The undoubted advantage of the obtained enamels is the wide interval of coat firing: from 820 to 940°C (an interval equal to 120°C). Furthermore, the fluorine-free coating withstands short-term heating up to 960 – 1000°C, which makes it possible to produce a high-quality one-layer direct-on coating using different methods of firing (gas firing, induction firing, etc.).

The developed enamels provide for good solubility of mineral filler in the melt in the amount of 5 – 20 weight parts (quartz sand, zirconium concentrate, pegmatite, feldspar, etc.), and in combination with low-melting milling additives (electrolytes) they produce low-melting phases in the form of a thin layer, wetting the metal surface and interrupting oxidation and gas reactions, which makes it possible to obtain a homogenous coating with uniform fine-bubble structure (d = 0.02 – 0.06 mm).

The preparation of fluorine-free enamel frits and production of coatings based on these frits are environmentally safe processes.

The coatings based on the synthesized fluorine-free enamels have higher resistance to the effect of aggressive media and better thermomechanical properties than the industrial compositions (Table 2), which makes it possible to substantially expand their application areas in protecting metals from corrosion. Pipes protected by coatings based on enamels ÉST-2 and ÉST-7 can be used in such sectors of industry as gas and oil extraction, chemical, carbon and oil-processing, shipbuilding, metallurgy, by-product coke industry, power, public services, and agriculture. Furthermore, pipes protected by fluorine-free enamels can be used, for instance, instead of stainless steel pipes of steel Kh18N10T (an expert evaluation of Kievaviaproekt Kiev Design Institute for Aircraft Industry authorized the replacement of a steel pipe by an enameled pipe in the aircraft fuel refining and preparation system at the Borispol International Airport).

The enamels have passed the technological and sanitary-hygienic tests and are approved by the sanitary authorities in Ukraine, which makes it possible to use them in drinking water supply systems and in food industry in production of sugar, wine, and other alimentary products. The fluorine-free enamels were also tested as enameling for steel pipes 57 – 273 mm in diameter and 6 – 12 m long intended

for service in cold and hot water supply systems and in oil and gas pipelines.

The deposition of enamel coating on the inner surface of pipes was carried out by the wet (slip) method, first, filling with slip the entire inner space of a vertically installed pipe and, then, releasing the slip from the pipe at the speed of 6 – 12 m/min.

The glass enamel coating was fired at 880 – 920°C as the pipe moved on rollers at the speed of 0.4 – 2 m/min with simultaneous rotation. The pipe heating duration depended on the pipe size and lasted 1.3 – 13.5 min. After firing, the glass enamel coating had a well-fused, defect-free surface with excellent luster and density.

Testing of pipes whose inner surface was protected by fluorine-free enamels indicated that the coatings are resistant to the effect of aggressive media with pH = 4 – 11 being transported at a speed up to 2 m/sec, with the pressure up to 10 MPa and the temperature ranging from – 60°C to + 90°C, and have good thermal resistance (up to 20°C) and high mechanical strength.

The fluorine-free enamels have been accepted for enameling of the inner surface of steel pipes at production enterprises in Ukraine and Russia.

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